

Analysis of Pt/SnO<sub>x</sub> During Catalysis of CO Oxidation

Paul A.Sermon, Valerie A.Self and E.P.S.Barrett  
Department of Chemistry, Brunel University, Uxbridge, Middx., UB8 3PH, UK

## SUMMARY

Temperature-programmed reduction using 6kPa H<sub>2</sub> suggests that a sample consisting of 3%Pt supported directly on SnO<sub>2</sub> is, under conditions of catalysis of CO oxidation used here, best represented as 3%Pt/SnO<sub>x</sub> since the support is likely to partially reduced, probably in the vicinity of the metal/oxide interface. Catalytic measurements at 421-424K show that this 3%Pt/SnO<sub>x</sub> is significantly more active per unit area of Pt than 6%Pt/SiO<sub>2</sub> in catalysing the oxidation of CO. In-situ micro-FTIR reveals that while the latter has predominantly linearly bound CO on the surface under reaction conditions, the Pt/SnO<sub>x</sub> also has a species absorbing at 2168cm<sup>-1</sup> which may be CO upon Pt in a positive oxidation state or weakly chemisorbed CO on zero-valent Pt. This may be directly involved in the low temperature oxidation of CO on the Pt/SnO<sub>x</sub> since being weakly held the activation energy for its surface diffusion to the metal/oxide interface will be low; such mobile species could allow the high rates of surface transport and an increase in the fraction of the surface over which the CO oxidation occurs. FTIR also reveals carbonate-type species on the P/SnO<sub>x</sub> surface.

## INTRODUCTION

Earlier papers by the present authors (ref.1,2) have illustrated the use of calorimetric, catalytic-activity and micro-FTIR measurements during CO oxidation on oxide-supported Pt catalysts. Here some of these analyses are applied to Pt/SnO<sub>x</sub> which are relevant to catalysts for the recombination of CO and O<sub>2</sub> in CO<sub>2</sub> lasers. It was a number of years ago that studies at Brunel (ref.3) showed that 2%Pd/SnO<sub>2</sub> was more active than 2%Pd/SiO<sub>2</sub> in that it achieved a given rate of CO oxidation at a temperature some 60K below that required on the silica-supported catalyst.

## CATALYSTS

EuroPt-1 Pt/SiO<sub>2</sub> has been described elsewhere (ref4). 3%Pt/SnO<sub>x</sub> was prepared by impregnation of the support with H<sub>2</sub>PtCl<sub>6</sub> (Johnson Matthey); after equilibration for 24h at room temperature, the catalyst was dried at 393K for 18h and then calcined at 773K for 6h.

While 1g of the reduced Pt/SiO<sub>2</sub> sample chemisorbed 168-188μmol H<sub>2</sub>, only 14.2μmol H<sub>2</sub> were chemisorbed on the same weight of Pt/SnO<sub>x</sub>, and furthermore this was very dependent upon the temperature of reductive pretreatment. This means that the Pt dispersion and surface area (58.2 m<sup>2</sup>/g) was rather modest for Pt/SnO<sub>x</sub> and may in future be greatly increased. Temperature-programmed reduction showed that the Pt in this catalyst promoted the reduction of the support at temperatures below those where the support alone would have reduced to give Pt/SnO<sub>x</sub> with x<2; it is likely that this reduction is predominantly at the metal-oxide interface.

## METHODS

The CO oxidation reaction was followed at 421-4K over 0.06-0.01g catalyst in a microflow reactor with a stream consisting of 1.64kPa CO and 1.78kPa O<sub>2</sub> with a N<sub>2</sub> balance to 101kPa which flowed at 21.1cm<sup>3</sup>/min; in in-situ micro-FTIR analysis the reactant partial pressures and flow rates were within 1.67kPa CO and 1.86kPa O<sub>2</sub>. Rates of CO oxidation were measured after reduction in H<sub>2</sub> at 423K for 30min and flushing in N<sub>2</sub> at the same temperature for 10min. Gas chromatography was used to determine product [CO<sub>2</sub>] concentrations at 10min intervals.

A spectra-Tech FTIR-PLAN microscope was used in conjunction with a Perkin Elmer 1710 FTIR spectrometer. Reflectance IR spectra were measured with a resolution of  $8\text{cm}^{-1}$  within a field of view of  $795\mu\text{m}$  and those for the surface before reaction subtracted.

## RESULTS

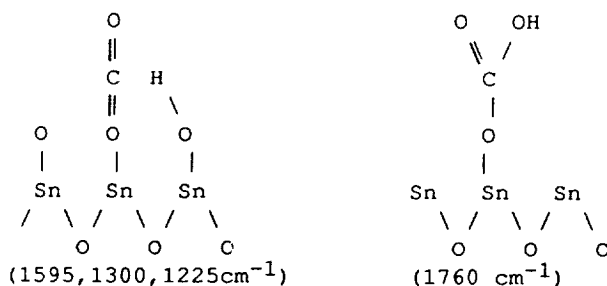
From Table 1 it is clear that per surface Pt atom detected by hydrogen chemisorption  $\text{Pt/SnO}_x$  is significantly more active than  $\text{Pt/SiO}_2$  at 423K.

**Table 1** Activities in CO oxidation (under conditions indicated in text)

T(K)	t(min)	%conversion CO	molCO/gPt/min	molec/Pt <sub>s</sub> /min	
424.1	20	8.72	1.31	0.26	Pt/SiO <sub>2</sub>
423.6	30	11.52	1.74	0.34	
423.2	40	17.80	2.67	0.52	
424.4	10	19.47	1.12	1.19	Pt/SnO <sub>x</sub>
421.5	20	29.23	1.69	1.79	
420.5	30	38.27	2.22	2.35	
420.5	40	30.97	1.79	1.90	
424.4	50	43.15	2.48	2.62	

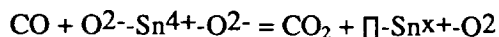
CO catalysis and chemisorption on Europt-1  $\text{Pt/SiO}_2$  revealed a peak at  $2080\text{cm}^{-1}$  corresponding to linearly-bound CO on the platinum surface (black band in Figure 1). However, in addition to this CO on  $\text{Pt/SnO}_x$  also showed a band at  $2168\text{cm}^{-1}$  (see hatched band Figure 1); in no case was there strong evidence of bridge-bound CO. This band at  $2168\text{cm}^{-1}$  on tin-oxide supported Pt is quite significant and further consideration will be given to this.

In addition during CO oxidation on  $\text{Pt/SnO}_x$  bicarbonate bands ( $1775, 1726, 1676, 1595, 1580, 1440\text{--}1490, 1320\text{--}1300$  and  $1275\text{cm}^{-1}$ ), were seen and these may correspond to bicarbonate species (ref.5) arising from adsorption of product  $\text{CO}_2$  on the hydroxylated  $\text{SnO}_x$ :



## DISCUSSION & CONCLUSIONS

It has been proposed (ref.3) that the mechanism of CO oxidation on  $\text{Pd/SnO}_x$  involves a synergy between the metal and the support with area around the interfacial contacts being active. CO may migrate from the metal to the oxide where additional oxidation occurs:



where oxygen vacancies in the  $\text{SnO}_x$  are then removed on direct  $\text{O}_2$  adsorption. The present  $\text{Pt/SnO}_x$  results are consistent with this picture and as a result per unit area of Pt,

Pt/SnO<sub>x</sub> is more active in the CO oxidation reaction than Pt/SiO<sub>2</sub> alone. Hydrogen chemisorption reveals the close interaction between the Pt and the SnO<sub>x</sub> with even mild reduction causing a loss of adsorption capacity as a result of SnO<sub>x</sub> decoration of the Pt in essentially a low temperature SMSI type process. In this context it is interesting that the binding energy for Pt upon silica (i.e. Pt 4f(7/2)=71.4eV) is lower than on SnO<sub>x</sub> (75eV), suggesting that the tin-oxide sustains the Pt thereon in a positive oxidation state. Equally, conductivity measurements show that Pt modifies the solid-state properties of the tin oxide.

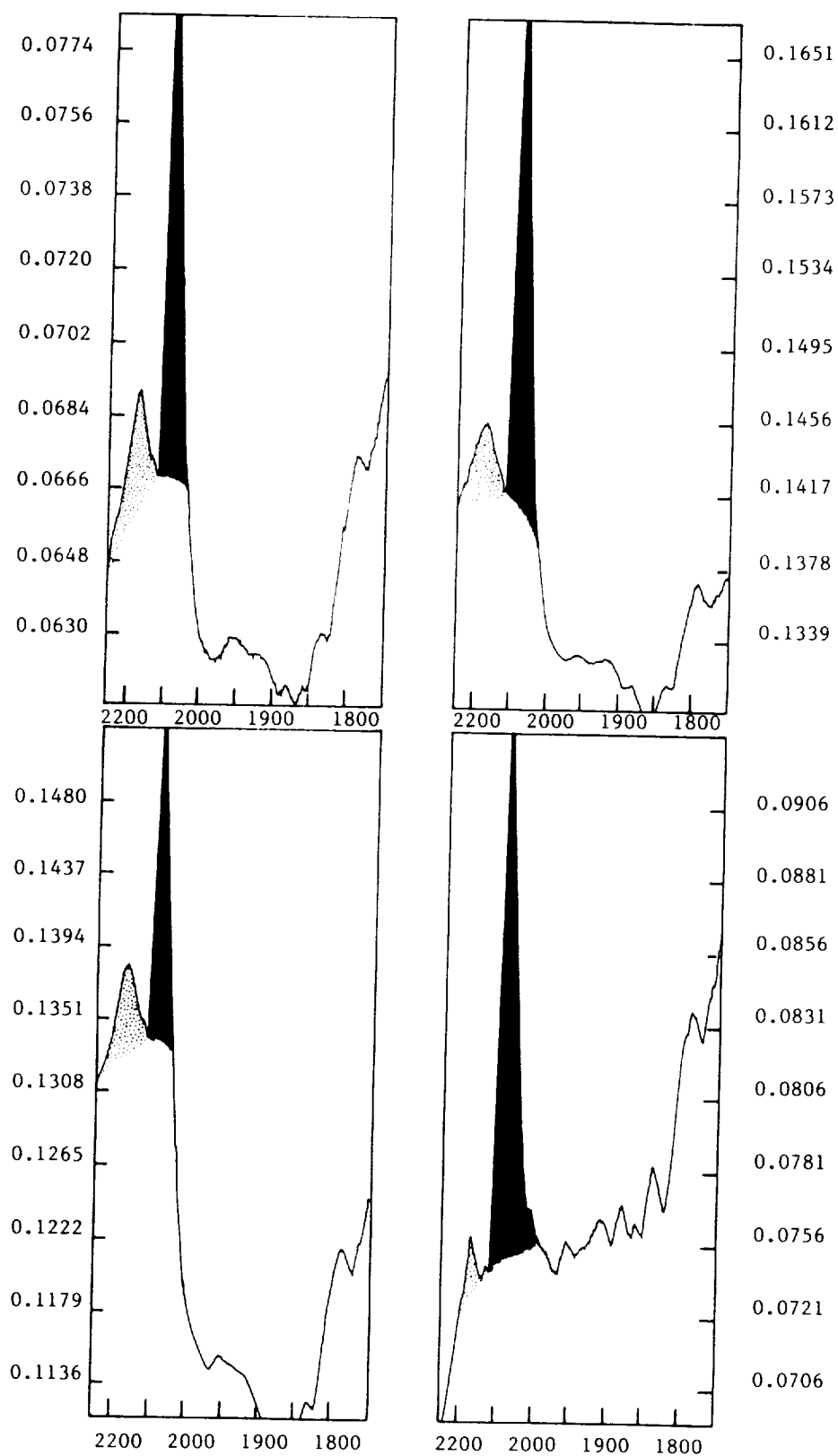
Clearly from Figure 1 in various parts of the Pt/SnO<sub>x</sub> surface the weakly-held CO has a concentration which is variable in comparison with the strongly-held CO, and so as one would expect there is surface heterogeneity. Consider now the mode of increase in CO oxidation activity and the surface species involved. FTIR reveals (in addition to linearly-bound CO (ref.6) an additional band at 2168cm<sup>-1</sup> which is close to that attributed to stretches for physically-held CO on Rh<sup>+</sup> (ref.7) or indeed even gaseous CO (2143cm<sup>-1</sup>); here we assume that this is weakly-held CO. It would be this CO which would *spillover* onto the supporting SnO<sub>x</sub> most easily and with the smallest activation energy barrier. Thus a weakly bound surface species may be directly involved in the accelerated oxidation on Pt/SnO<sub>x</sub> in line with earlier postulates (ref.8).

#### ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of VAS by SERC.

#### REFERENCES

1. P.A. Sermon, V.A. Self, M.S.W. Vong, A.T. Wurie and N.D. Hoyle, (1st NASA paper at 1989 meeting).
2. V.A. Self and P.A. Sermon, (2nd NASA paper at 1989 meeting).
3. G.C. Bond, L.R. Molloy and M.J. Fuller, J. Chem. Soc. Chem. Commun., 796, (1975).
4. A. Frennet and P.B. Wells, Appl. Catal., 18, 243, (1985).
5. E.W. Thornton and P.G. Harrison, Trans. Far. Soc., year, vol, 461.
6. A. Crossley and D.A. King, Surf. Sci., (1977), 68, 528; Surf. Sci., (1980), 95, 131; S.R. Bare, P. Hofman and D.A. King, Surf. Sci., (1984), 144, 347; R.P. Eischens and W.A. Pliskins, Adv. Catal., (1958), 10, 1; G. Blyholder, J. Phys. Chem., (1964), 68, 2772.
7. J.T. Yates and G.L. Haller, J. Phys. Chem., (1984), 88, 4660.
8. D.A. Dowden, Annual Reports on Progress of Chemistry C in, 1979, (1980), 76, 3, (RSC).



**Figure 1** Reflectance FTIR for weakly-held (hatched) and linearly-bonded (black) surface-CO species during CO oxidation on Pt/SnO<sub>x</sub> at measured in different segments of its surface